

PATENT SPECIFICATION

(11) 1 530 445

1 530 445

- (21) Application No. 1069/75 (22) Filed 10 Jan. 1975
(23) Complete Specification filed 9 Jan. 1976
(44) Complete Specification published 1 Nov. 1978
(51) INT CL² C08F 4/02, 4/64, 10/00
(52) Index at acceptance
B1E 341 34Y 360 36Y 370 37Y 491 49Y 550 55Y 579 580
584 590 652 661 754 755 75Y 760 78X 78Y
C3P 404 440 452 464 474 486 578 582 584 590 592 598 602
GA
(72) Inventors JOHN GABRIEL SPEAKMAN and PREM SAGAR
THUKRAL



(54) POLYMERISATION CATALYST

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, EC2Y 9BU, a British company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the production of a supported Ziegler catalyst and to the use of the catalyst in the polymerisation of olefins.

It has long been known that 1-olefins such as ethylene can be polymerised by contacting them under polymerisation conditions with a catalyst obtained by activating a transition metal-containing catalyst component, e.g. a titanium compound such as titanium tetrachloride, with an activator i.e. a co-catalyst, e.g. an organo-metallic compound such as triethylaluminium. These transition metal-containing catalysts are generally referred to in the art as "Ziegler catalysts".

According to the present invention there is provided a process for the production of a supported Ziegler catalyst component comprising forming a catalyst base by exposing a mixture of a support material comprising an inorganic oxide or elementary carbon and a magnesium compound to microwave radiation to heat the mixture to an apparent temperature (as herein defined) of at least 100°C, and incorporating a transition metal compound therein.

The invention further provides a process for polymerising 1-olefins comprising contacting the monomeric olefin with the supported Ziegler catalyst component of the present invention in the presence of a Ziegler catalyst activator.

The support material employed in the present invention is suitably any particulate inorganic oxide or elementary carbon. Preferred inorganic oxides are those that are commonly referred to in the art as being

"difficultly reducible inorganic oxides". Oxides of this type include, for example, silica, alumina, zirconia and thoria and mixtures or composites of such oxides, for example silica-alumina. Examples of elementary carbon support materials suitable for use in the present invention are gas carbon, wood charcoal, animal charcoal, graphite and carbon black. Mixtures of inorganic oxides with graphite or carbon black are preferred as they are good absorbers of microwaves.

The support materials preferably have a surface area in the range 20 to 3,000 square meters per gram and most preferably 100 to 500 square metres per gram as measured by the well known B.E.T. method. They preferably have a mean particle diameter in the range 0.05 to 1,000 μm , most preferably 50 to 200 μm , and a porosity in the range 0.1 to 10.0, most preferably 1.0 to 2.5 millilitres per gram as measured by the technique of water porosimetry.

Particularly preferred support materials are dried microspherical silica gels and carbon black.

The magnesium compound employed in the present invention is suitably magnesium oxide, magnesium hydroxide, a magnesium salt, for example magnesium chloride, magnesium carbonate, magnesium sulphate or magnesium nitrate, or an alkoxide, for example magnesium ethoxide. Magnesium chloride is preferred, particularly the anhydrous material.

It is preferred that either the support material or the magnesium compound (or both) should be a good absorber of microwave radiation. If a given mixture according to the invention is found to be a poor microwave absorber, it is preferred to add to the mixture an inert material which is known to be a good absorber of microwaves. By an inert material is meant a material which does not have a deleterious effect upon Ziegler catalysts.

The microwave radiation employed in the present invention suitably has a frequency

or frequency band in the range 100—300,000 M Hertz (i.e. from 0.1 to 300 mm in wavelength). The radiation preferably has a frequency in the range 100 to 5000 M Hertz.

- 5 Commercial microwave sources, such as microwave ovens, which normally have a frequency of 900 or 2,450 MHz in the U.K. can be suitably employed in the invention.

- 10 The power of the microwave radiation employed is suitably in the range 0.01 to 20 kW per kilogramme of mixture employed. The exposure is suitably sufficient to give an apparent treatment temperature in the range 100 to 2,000°C, preferably 150 to 800°C for
15 a period of time in the range 1 minute to 8 hours. Measurement of the actual temperature of a substance in the presence of microwaves presents problems due, to inter alia, absorption of microwave energy by the temperature
20 detecting device. Accordingly the term apparent temperature is used to denote the temperature of the mixture is measured by any conventional technique in the absence of microwave radiation. This can be determined
25 in a trial run at any instant, for example, by disconnecting the microwave source, plotting the cooling curve of the mixture and extrapolating back to the instant that the source was disconnected.

- 30 The transition metal compound used in making the catalyst of the present invention may be any of the transition metal compounds known to be useful in forming Ziegler catalysts. Examples of such compounds are the
35 halides, oxyhalides, halo-alkoxides and alkoxides of the metals of groups IVa, Va and VIa of the Periodic Table. Particularly preferred are titanium compounds having the formula $Ti(OR)_nCl_{4-n}$ wherein R is an alkyl
40 group having 1 to 6 carbon atoms and n has any value from 0 to 4 inclusive, for example, $TiCl_4$, $Ti(OEt)_4$, $Ti(OiPr)_4$, $Ti(OEt)_3Cl$ and $Ti(OiPr)_2Cl_2$. Titanium oxychloride ($TiOCl_2$) is an example of a suitable oxyhalide.

- 45 The quantity of magnesium compound employed in the process of the present invention is suitably sufficient to give a magnesium concentration in the range of 0.5 to 20%, preferably
50 3 to 10% based on the weight of the support material.

- The quantity of transition metal compound is suitably sufficient to give a concentration of transition metal in the range 0.5 to 20%, preferably 4 to 10% based on the total catalyst
55 weight.

- The magnesium compound and the support material are preferably formed into an intimate mixture before or during the exposure to microwaves. The mixture can be formed for
60 example by mixing the support material with the dry magnesium compound and if desired, grinding or milling the mixture; by shaking together or fluidising the support material and the powdered magnesium compound; by
65 adding a solution of the magnesium compound

in an inert volatile solvent (e.g. water, hydrocarbon, ether, alcohol or ester) to the support material and volatilising the solvent; or by melting the magnesium compound in the presence of the support material and pulverising the melt or the solidified melt. When the magnesium compound employed is magnesium chloride it is preferred to dry mix the support material and magnesium chloride and expose the mixture to microwaves in a fluidised
70 bed.

It is preferred to expose the mixture of the magnesium compound and the support material to microwaves under fluidised bed conditions and under such conditions the fluidising gas can be any suitable gas that does not have a deleterious effect on the final catalyst. The fluidising gas is preferably a dry inert gas such as nitrogen.

The catalyst base must be substantially free from water prior to incorporation of the transition metal compound.

The transition metal compound can be incorporated into the catalyst base in any convenient manner. Preferably, the catalyst base and the transition metal compound are heated together (using conventional heating techniques or microwave radiation) at a temperature in the range 50 to 200°C. This can be carried out for example by heating a mixture of the catalyst base and the transition metal compound, or by heating the catalyst base and the transition metal compound together in a refluxing inert diluent or in a refluxing solvent for the transition metal compound; or by passing the vapour of a volatile transition metal compound into a heated bed, e.g. a fluidised bed, of the catalyst base. It is preferred to heat the transition metal compound and the catalyst base at a temperature in the range 70 to 100°C for $\frac{1}{2}$ to 5 hours in the presence of an inert diluent or a solvent for the transition metal compound. Suitable inert diluents (which are in some cases also solvents for the transition metal compound) are, for example, saturated aliphatic hydrocarbons such as petroleum ether, butane, pentane, hexane, heptane, methyl-cyclohexane and aromatic hydrocarbons such as benzene, toluene or xylene.

Any excess transition metal compound remaining in the catalyst component after the incorporation step is preferably removed therefrom, for example by solvent washing, distillation or any other convenient technique which does not have a deleterious effect on the catalyst. Excess titanium compounds having the formula $Ti(OR)_nCl_{4-n}$ has hereinbefore described can be conveniently removed by washing the catalyst several times with solvent such as, for example, those listed in the previous paragraph.

The incorporation of the transition metal compound into the catalyst base should be carried out in the substantial absence of oxygen or moisture.

70

75

80

85

90

95

100

105

110

115

120

125

130

As is the case with other supported Ziegler catalysts, the catalyst component of the present invention requires activation with a co-catalyst, i.e. a Ziegler catalyst activator. Ziegler catalyst

5 activators and the methods in which they are used to activate Ziegler catalysts are well known. Examples of Ziegler catalyst activators are organic derivatives, or hydrides of metals of groups I, II, III and IV of the Periodic

10 Table. Particularly preferred are trialkylaluminium compounds or alkylaluminium halides, for example triethylaluminium, tributylaluminium and diethylaluminium chloride.

15 The polymerisation process of the present invention can be applied to the homopolymerisation of 1-olefins, e.g. ethylene or propylene, or to the copolymerisation of mixtures of 1-olefins, e.g. ethylene with propylene,

20 1-butene, 1-pentene, 1-hexene, 4-methylpentene-1, 1,3-butadiene or isoprene. The process is particularly suitable for the homopolymerisation of ethylene or the copolymerisation of ethylene with up to 40% by weight

25 (based on total monomer) of comonomers.

The polymerisation conditions can be in accordance with known techniques used in supported Ziegler polymerisation. The polymerisation can be carried out in the gaseous

30 phase or in the presence of a dispersion medium in which the monomer is soluble. As a liquid dispersion medium, use can be made of an inert hydrocarbon which is liquid under the polymerisation conditions, or of the monomer or monomers themselves maintained

35 in the liquid state under their saturation pressure. The polymerisation can if desired be carried out in the presence of hydrogen gas or other chain transfer agent to vary the molecular weight of the produced polymer.

The polymerisation is preferably carried out under conditions such that the polymer is formed as solid particles suspended in a liquid

40 diluent. Generally the diluent is selected from paraffins and cycloparaffins having from 3—30 carbon atoms per molecule. Suitable diluents include for example isopentane, isobutane and cyclohexane. Isobutane is preferred.

Methods of recovering the product polyolefin are well-known in the art.

The process of the present invention can be used to make the supported Ziegler catalyst component at high throughput rates.

The polymerisation catalyst of the present invention can be used to make high density ethylene polymers and copolymers at high productivity having properties which render them suitable for injection moulding.

The invention is further illustrated by the following Examples:—

60 In the Examples the melt index ($MI_{2.16}$) and high load melt index ($MI_{12.6}$) were determined according to ASTM method 1238 using 2.16 kg and 21.6 kg loads respec-

tively; the units are grammes per 10 minutes. 65
The melt index ratio (MIR) is $MI_{2.16}/MI_{12.6}$.

Example 1.

Preparation of a catalyst on $MgCl_2$ /Silica.

19.08g Davison Grade 951 Silica (previously dried overnight in a vacuum oven at 150°C), 11.64g anhydrous $MgCl_2$ (B.D.H. technical grade) (previously dried overnight in a vacuum oven at 150°C) and 1.4ml of distilled water were thoroughly mixed then

70 charged to a microwave oven. The sample was subjected to 2450 MHz radiation at a power of 66W for 60 minutes. The temperature of the sample rose to 185°C.

75

The catalyst support was stored under dry nitrogen and all subsequent operations were carried out under an atmosphere of dry nitrogen.

80

The support was slurried with 100ml dry, deoxygenated cyclohexane, then 5ml (65m moles) isopropanol, 50 ml (168m moles) titanium tetraisopropylate and 20ml (182 m moles) titanium tetrachloride were added. The mixture was refluxed for 2 hours. The supernatant liquid was decanted off and the solid material washed with 40ml dry cyclohexane, the washings being removed by decanting. Washing and decanting were repeated 10 times. Finally a slurry of the catalyst component in cyclohexane was made up with a solids content of 126.4 mg/ml. The slurry

85 90 95

was used to polymerise ethylene as shown below.

Example 2.

Preparation of a catalyst on $Mg(OEt)_2$ /Silica.

19.51g Davison Grade 951 silica (previously dried overnight in a vacuum oven at 150°C) and 15.10g $Mg(OEt)_2$ were thoroughly mixed then charged to a microwave oven. The sample was subjected to 2450 MHz radiation at a power of 44K for 26 minutes, then at a power of 66W for 36 minutes. The temperature of the sample rose to 280°C.

100 105

The catalyst support was stored under dry nitrogen and all subsequent operations were carried out under an atmosphere of dry nitrogen.

110

8.33g of the support were slurried with 100ml dry deoxygenated cyclohexane then 5ml (65m moles) isopropanol, 50ml (168m moles) titanium tetraisopropylate and 20ml (182 m moles) titanium tetrachloride were added. The mixture was refluxed for 2 hours. The supernatant liquid was decanted off and the solid material washed with 40ml dry cyclohexane, the washings being removed by decanting. Washing and decanting were repeated 10 times. Finally a slurry of the catalyst component in cyclohexane was made up with a solids content of 7.58 mg/ml. The slurry

115 120 125

was used to polymerise ethylene as shown below.

Example 3.

Polymerisation of Ethylene.

The polymerisations were carried out in a ½ gallon stainless steel stirred autoclave. The slurry was added with a syringe to the reactor purged with nitrogen and maintained at 30–40°C. Aluminium tri-isobutyl was then added in a 25% by weight solution in cyclohexane, followed by ~500 ml isobutane diluent. The reactor was heated until the pressure of the isobutane reached 100 p.s.i.g.

(~58°C) when hydrogen was added if required. Further heating brought the reactor to the polymerisation temperature when ethylene was added to bring the total pressure of the reactor content to 600 p.s.i.g. The polymerisation conditions and results are summarised in the Table. Examples 1a–1e were carried out using catalyst as prepared in Example 1, and Examples 2a and 2b using catalyst from Example 2.

TABLE

Example	Solid catalyst component weight (mg)	Wt(mg) of Al(Bu) ³	Partial Pressure (psi) of H ₂ of C ₂ H ₄	Run length (min)	Catalyst Productivity (hour ⁻¹)	MI _{2.16}	MIR	Remarks
1a	126	786	0	14	2040	8750		MI _{2.1-6} too low to measure.
1b	126	786	130	60	2620	2620	5.49	
1c	101	786	150	60	2300	2300	11.9	
2a	76	786	0	60	3770	3770	27.3	MI _{2.1-6} too low to measure.
2b	152	786	130	60	664	664	4.45	
			245	60			32.4	

N.B. All reactions carried out at 90°C except Example 1c where the temperature was 85–107°C.

WHAT WE CLAIM IS:—

1. A process for the production of a supported Ziegler catalyst component comprising forming a catalyst base by exposing a mixture of a support material comprising an inorganic oxide or elementary carbon and a magnesium compound to microwave radiation to heat the mixture to an apparent temperature (as herein defined) of at least 100°C, and incorporating a transition metal compound therein.
2. A process as claimed in Claim 1 wherein the support material comprises silica, alumina, zirconia or thoria as the inorganic oxide.
3. A process as claimed in Claim 1 wherein the support material comprises graphite or carbon black as the elementary carbon.
4. A process as claimed in any one of the preceding claims wherein the magnesium compound is magnesium chloride.
5. A process as claimed in any one of the preceding claims wherein the microwave radiation has a frequency in the range 100 to 5000 MHz.
6. A process as claimed in any one of the preceding claims wherein the apparent treatment temperature is in the range 150 to 800°C.
7. A process as claimed in any one of the preceding claims wherein the transition metal compound is a titanium compound.
8. A process as claimed in Claim 7 wherein the titanium compound has the general

formula $Ti(OR)_nCl_{3-n}$ and wherein R is an alkyl group having 1 to 6 carbon atoms and n has any value from 0 to 4 inclusive.

9. A process as claimed in any one of the preceding claims wherein the quantity of magnesium compound employed is sufficient to give a magnesium concentration in the range 0.5 to 20% based on the weight of the support material.

10. A process for the production of a supported Ziegler catalyst component substantially as hereinbefore described in the Examples.

11. A supported Ziegler catalyst component whenever prepared by the process claimed in any one of the preceding claims.

12. A process for the polymerisation of 1-olefins comprising contacting the monomeric olefin with the supported Ziegler catalyst component as claimed in Claim 11 in the presence of a Ziegler catalyst activator.

13. A process as claimed in Claim 12 wherein the Ziegler catalyst activator is a trialkylaluminium.

14. A process for the preparation of polyethylene substantially as hereinbefore described in the Examples.

15. Polyolefins whenever prepared by the process claimed in Claims 12, 13 or 14.

J. HARRY,
Agent for the Applicants.